

Comparison of thermal behaviour of γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in oxidative and inert media

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Received December, 2014; Revised January, 2015

The aim of the present study is to investigate and compare the decomposition mechanism of the slightly known γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in oxidative and inert media under non-isothermal conditions with analysis of the evolved gases. Pure phase of pinkish orthorhombic dihydrate was obtained and characterized by X-ray diffraction and scanning electron microscopy. The non-isothermal investigation was carried out in static air and dynamic Ar atmosphere (60 ml min^{-1}) at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ in the range of $25\text{--}800 \text{ }^\circ\text{C}$, using a coupling system TG-MS – instrument SETSYS2400 combined with a mass-spectrometer. According to TG-DTA-DTG curves, dehydration proceeds in the interval $140\text{--}187 \text{ }^\circ\text{C}$ in Ar and $140\text{--}182 \text{ }^\circ\text{C}$ in air. The corresponding intervals of decomposition are $335\text{--}434 \text{ }^\circ\text{C}$ in Ar and $230\text{--}361 \text{ }^\circ\text{C}$ in air. In inert Ar atmosphere, CO and CO_2 are liberated simultaneously and MnO is obtained as a final product. In oxidative air atmosphere the evolved CO participate in additional oxy-reduction reactions and only CO_2 is detected. The decomposition is accompanied by oxidation of Mn(II) thus leading to formation of manganese oxides in higher and most probably mixed oxidation states.

Keywords: manganese(II) oxalate; decomposition, thermal analyses, XRD, SEM.

INTRODUCTION

Sparingly soluble manganese oxalate is widely used nowadays as a precursor for various nano-sized manganese oxides with a variety of technological applications due to their magnetic, electric and catalytic properties [1, 2, 3]. The widespread use of manganese oxides and the dependence of their properties on composition explain the interest in studying the process of thermal decomposition of manganese oxalate. A specific feature of this system is the simultaneous liberation of CO_2 and CO, the latter being able to reduce the obtained oxide.

Recently, three crystal forms of manganese oxalate are known – monoclinic α - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (SG C2/c) [4], orthorhombic γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (P2₁2₁2₁) [5] and orthorhombic trihydrate $\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Pcca) [6]. While the mechanism and products of

thermal decomposition of monoclinic dihydrate in air have been extensively studied by various methods [7–12], the literature data for the trihydrate and orthorhombic dihydrate are quite scarce – [12, 13] and [14], respectively, as well as our papers [15, 16]. Our previous investigations [15] revealed that the difference in the crystal lattice of α - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ is responsible for both the different thermal behavior of the materials and the different extent of Mn(II) oxidation. In the present study, we focused on the crystal form γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The mechanism of its thermal decomposition is investigated and a comparison between its behavior in air and in Ar atmosphere is performed on the basis of thermal analysis data.

EXPERIMENTAL

Manganese oxalate was synthesized by mixing $\text{Mn}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solutions at room temperature. The obtained precipitate was kept for 8 hours at $60 \text{ }^\circ\text{C}$ and magnetically steered. The pinkish

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product $\gamma\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ was filtered, washed several times and dried in a desiccator.

Orthorhombic $\gamma\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ was investigated by X-ray diffraction using a D 500 Siemens powder diffractometer with $\text{Cu K}\alpha$ radiation. The phase identification was performed by the JCPDS data-base. The morphological characterization was carried out by a scanning electron microscope (SEM) JEOL JSM-5510. The thermal investigation was performed in both static air and Ar flow (60 ml min^{-1}) on a sample of mass about 15 mg, with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in the range of $25\text{--}800\text{ }^\circ\text{C}$, using a coupling system TG-MS – instrument SETSYS2400 (SETARAM, France) for thermal analysis and OmniStar mass spectrometer.

RESULTS AND DISCUSSION

The X-ray pattern is presented in Fig. 1 (a) and confirms that as synthesized product is a pure phase of $\gamma\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (JPCDS 32-0647). The strongest reflections of $\text{MnC}_2\text{O}_4\cdot 3\text{H}_2\text{O}$ (13.323 deg) and of $\alpha\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (18.430 deg) were not observed. The high intensities and small FWHM of the diffraction peaks indicate a good crystallinity of the sample. The scanning electron microscope image of the sample (Fig. 1, b) shows a rod-shape of the crystals. Due to the long duration of magnetic stirring, the rods of oxalate are fragmented and with uneven walls, but their prismatic shape is clearly visible.

Figure 2 shows the TG/DTA curves in air and in Ar at a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The evolved

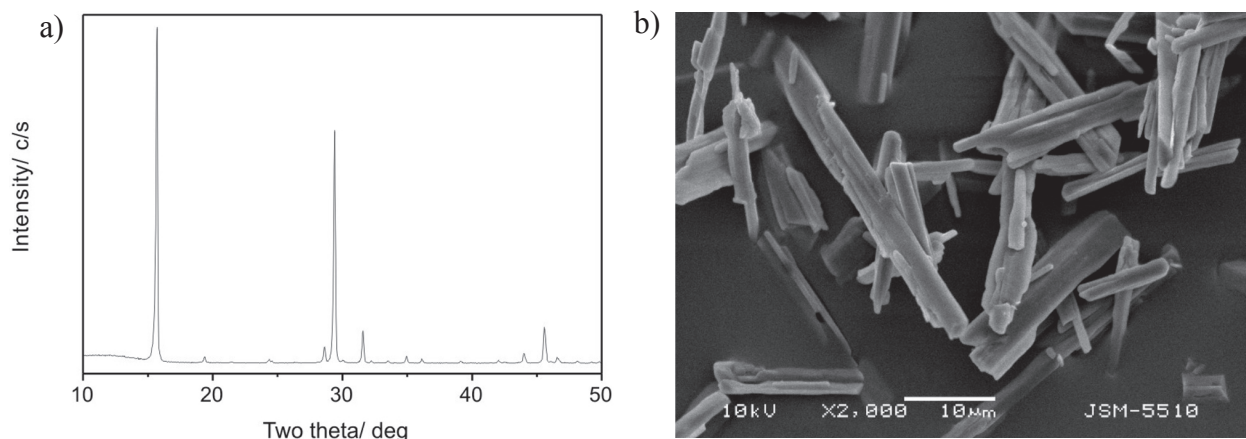


Fig. 1. XRD pattern (a) and scanning electron micrograph of $\gamma\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (b)

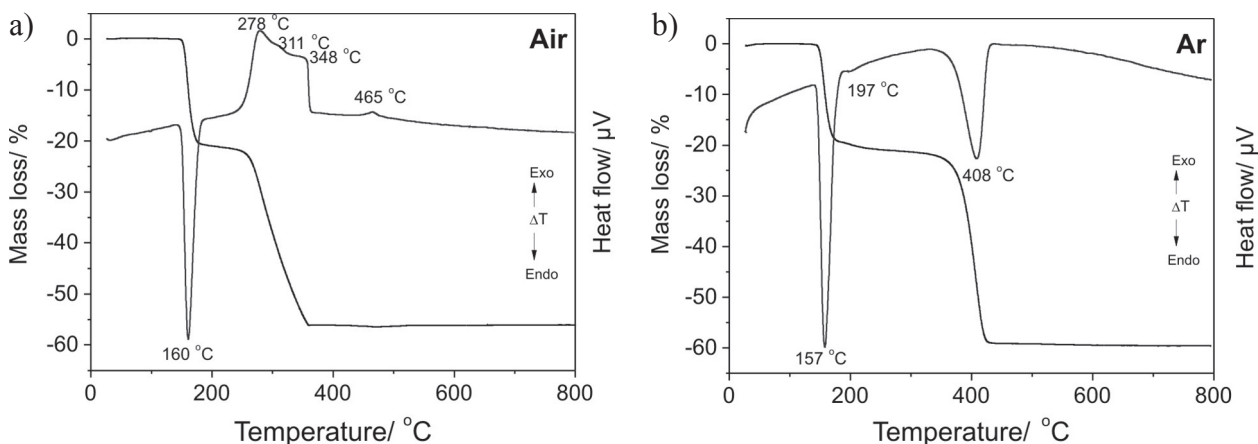


Fig. 2. DTA and TG curves of $\gamma\text{-MnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ decomposition in air (a) and Ar (b)

gases are depicted on Fig. 3. As expected, for $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ the temperature of dehydration is almost the same in both media, with peaks position at 156 °C in Ar and 160 °C in air. The dehydration occurs in a single step as in the case of monoclinic α - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [15]. The theoretical mass loss (ML_{th}) is 20% and the observed experimental values (ML_{exp}) at the end of the steep slope of TG-curves in Ar and air are 19,3% and 20,6%, respectively.

The decomposition process is carried out after dehydration and the temperature of decomposition depends on the kind of atmosphere, in which the process is occurred and on the inclination of the Mn(II) to be oxidized. It is known that in air, oxidation of Mn(II) to Mn(III) takes place just before decomposition and catalyzes the latter [7, 8, 11, 17]. Accordingly, the decomposition in Ar starts at 325 °C, a much higher temperature than in air and one narrow endo-thermal peak is observed at 408 °C. In oxidative medium (air), the decomposition starts at 227 °C and results in several exo- and endo-thermal peaks at 278, 311 and 348 °C. The DTA curve is more complicated due to the overlapping of the

processes of decomposition, oxidation of Mn(II) to higher oxidation states Mn^{n+} and a subsequent reduction to Mn^{m+} . The above statements are supported by evolution curves of the liberated during decomposition gases (Fig. 3). In Ar atmosphere CO and CO_2 are liberated simultaneously in the narrow interval of 325 to 449 °C with peaks of the symmetric curves at 408 °C, while in air only CO_2 evolution is observed which starts at much lower temperature. The lack of CO evolution as well as the consumption of O_2 in this region (not shown) indicates that CO oxidation takes place during the decomposition, most probably catalyzed by Mn^{n+} and Mn^{m+} [8] available in the system. This leads to the broad asymmetric curve of CO_2 evolution and implies that the CO oxidation contributes to the complicated trend of the DTA curve.

The experimentally measured mass losses at the end of decomposition in Ar and air are 59,1% and 56,3%, respectively. The theoretical values for obtaining of different manganese oxides are 51,4% (MnO_2), 55,04% (Mn_5O_8), 55,9% (Mn_2O_3), 57,38% (Mn_3O_4), and 60,35% (MnO). Based on the observed

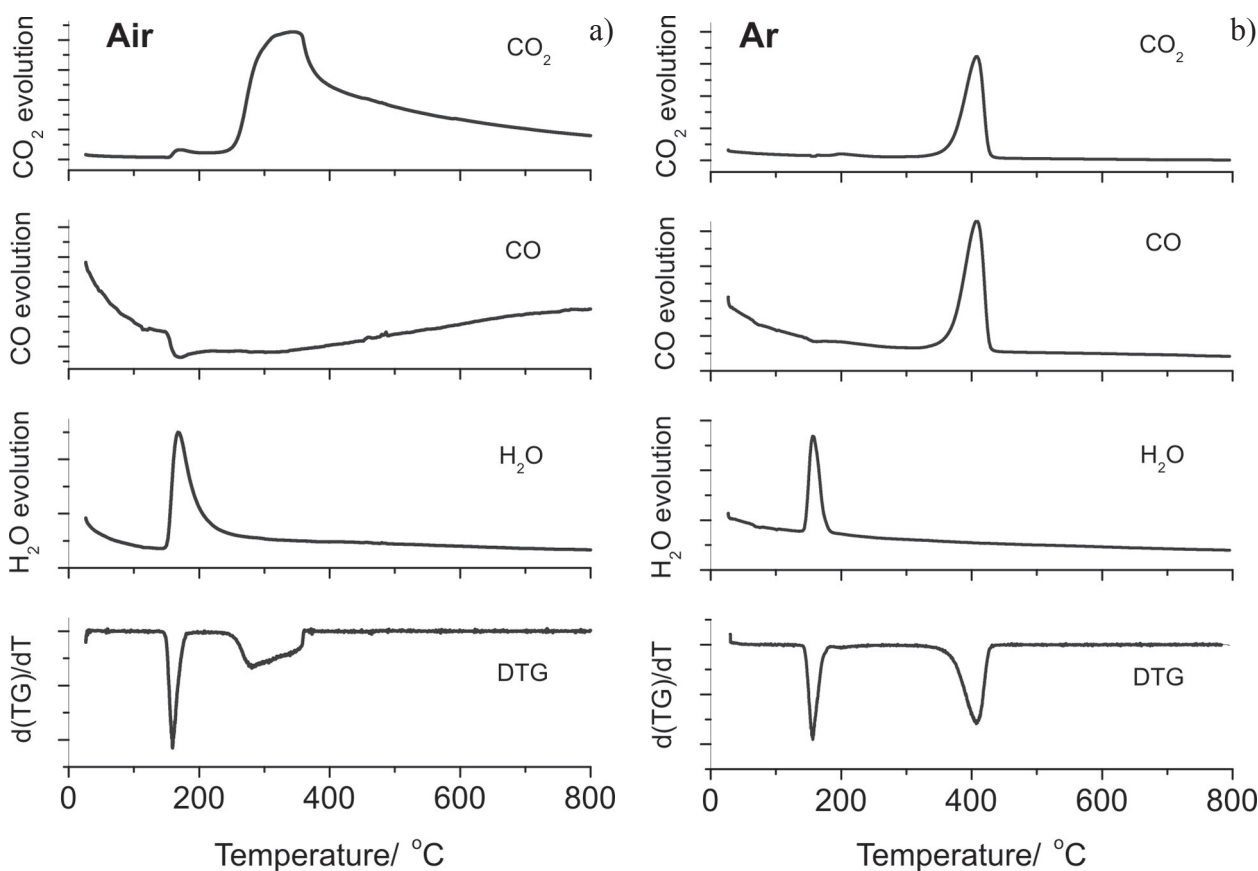


Fig. 3. DTG and evolution curves of H_2O , CO and CO_2 in air (a) and Ar (b)

ML_{exp} and the green color of the final product, one can conclude that in Ar atmosphere the decomposition of γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ leads to the formation of MnO. In air probably mixture of oxides Mn_2O_3 and Mn_3O_4 is produced, but it is difficult to define the products only on the basis of TG analysis because of the complexity of the system. For understanding of the phenomena additional studies by other methods are necessary to be performed.

CONCLUSIONS

Thermal decomposition of γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in both air and Ar was investigated and compared. Data for the evolved gases during decomposition of this crystal form of manganese oxalate is reported for the first time. According to TG-DTA-DTG curves, dehydration proceeds in the interval 140–187 °C in Ar and 140–182 °C in air. The corresponding intervals of decomposition are 335–434 °C in Ar and 230–361 °C in air. In Ar atmosphere, CO and CO_2 are liberated simultaneously and MnO is obtained as a final product. In oxidative air atmosphere the evolved CO participate in additional oxy-reduction reactions and only CO_2 is detected. The decomposition is accompanied by oxidation of Mn(II) leading to the formation of manganese oxides in higher and most probably mixed oxidation states. The investigations at other heating rates and calculation of the reaction enthalpy and activation energy of the processes under different atmospheres are in progress.

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СЪПОСТАВЯНЕ НА ТЕРМИЧНОТО ПОВЕДЕНИЕ НА γ -MnC₂O₄·2H₂O В ОКИСЛИТЕЛНА И ИНЕРТНА АТМОСФЕРА

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Постъпила декември, 2014 г.; приета януари, 2015 г.

(Резюме)

Цел на представената работа е изследване и съпоставяне на процеса на неизотермично разлагане на слабо изучения γ -MnC₂O₄·2H₂O в окислителна и инертна атмосфера, съпроводено с анализ на отделените газове. Полученият орторомбичен дихидрат е охарактеризиран посредством рентгенова дифракция и сканираща електронна микроскопия. Изследването при неизотермични условия е проведено в среда от статичен въздух и продухвач Ar (60 ml min⁻¹) в температурен интервал 25–800 °C при скорост на нагряване 5 °C min⁻¹. Използван е TG-MS – апарат SETSYS2400, комбиниран с мас-спектрометър. Съгласно TG-DTA-DTG кривите, в Ar атмосфера дехидратацията протича в интервала 140–187 °C, а разлагането в интервала 335–434 °C. Съответните температурни интервали в среда на въздух са 140–182 °C и 230–361 °C. В инертната Ar среда е установено едновременно отделяне на CO и CO₂ в хода на разлагане на оксалата, като крайният продукт е MnO. В окислителна среда отделяният се при разлагане CO участва в допълнителни окислително-редукционни процеси, поради което се регистрира единствено отделяне на CO₂. Процесът на разлагане на γ -MnC₂O₄·2H₂O в тази среда е съпроводен с окисление на Mn(II), водещо до получаване на оксиди, в които манганът е в по-високи и най-вероятно смесени окислителни състояния.